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Compounds containing λ^3,σ^2-Sb=C bonds: synthesis and structural characterisation of the first stiba-enol, Mes*C(O)Sb=C(OH)Mes* (Mes* = $C_6H_2Bu^t{}_3$-2,4,6) and a 2,3-distibabutadiene, {Mes(Me_3SiO)C=Sb}$_2$ (Mes = $C_6H_2Me_3$-2,4,6) †

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The reactions of [Li{Sb($SiMe_3$)$_2$}] with RCOCl, R = $C_6H_2Bu^t{}_3$-2,4,6 (Mes*) or $C_6H_2Me_3$-2,4,6 (Mes), afford mixtures of the 2,3-distibabutadienes, {R(Me_3SiO)C=Sb}$_2$, and the 2-stiba-1,3-dionatolithium complexes, [Li{OC(R)SbC(R)O}(DME)$_n$], *n* = 1 or 0.5, the latter of which (R = Mes*) can be protonated to give the first stiba-enol, Mes*C(O)Sb=C(OH)Mes*, which has been structurally characterised.

Since the preparation of the first thermally stable phosphaalkyne, P≡CBu^t, in 1981 the field of low coordination phosphorus chemistry has become well established.[1] Not surprisingly, the chemistry of compounds containing As–C multiple bonds was slower to develop but is now relatively well explored.[2] By contrast, there is a paucity of knowledge of analogous low coordination antimony compounds which probably results from their inherent thermal instability. In fact, to date there is only one structurally characterised example of a compound, {R(Me_3SiO)C=Sb}$_2$ **1** [R = $C_6H_2Bu^t{}_3$-2,4,6 (Mes*)], that contains largely localised Sb–C double bonds,[3] though related compounds have recently been implicated as reactive intermediates in the formation of stibacycles.[4] This remarkably stable compound was prepared in low yield from the reaction of Mes*COCl with [Li{Sb($SiMe_3$)$_2$}], a surprising result considering that the analogous reaction of Bu^{t}COCl with [Li{Sb($SiMe_3$)$_2$}] affords a high yield of the delocalised 2-stiba-1,3-dionatolithium complex, [{[Li{OC(Bu^t)SbC(Bu^t)O}(DME)$_{0.5}$]$_2$}$_\infty$],[5] the coordination chemistry of which we are currently investigating.[6] Herein we report that a stibadionatolithium complex is, indeed, the major reaction product in the preparation of **1** and that a similar product mixture is obtained in the reaction of the less hindered acyl chloride MesCOCl (Mes = $C_6H_2Me_3$-2,4,6) with [Li{Sb($SiMe_3$)$_2$}]. In addition, this work has led to the synthesis and structural characterisation of the first stiba-enol which, in the solid state, contains a rare example of a localised Sb–C double bond.

The product mixtures obtained from the treatment of [Li{Sb($SiMe_3$)$_2$}] with 1 equivalent of either Mes*COCl or MesCOCl were extracted with hexane to give the distibabutadienes, **1** and **2**, in low yield (18% and 5% respectively) after concentration of the extracts (Scheme 1). The hexane insoluble fractions of the reaction mixtures were further extracted with diethyl ether affording the 2-stiba-1,3-dionatolithium complexes, **3** and **4**, in moderate yields (38% and 45%) after recrystallisation. Treatment of a diethyl ether solution of **3** with 1 equivalent of anhydrous HCl, followed by recrystallisation from diethyl ether gave red crystals of the light sensitive stiba-enol, **5**, in high yield (97%).

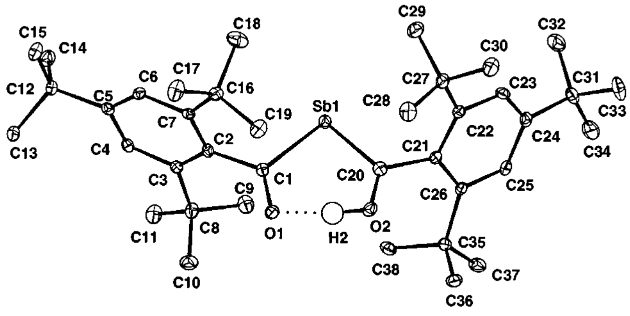
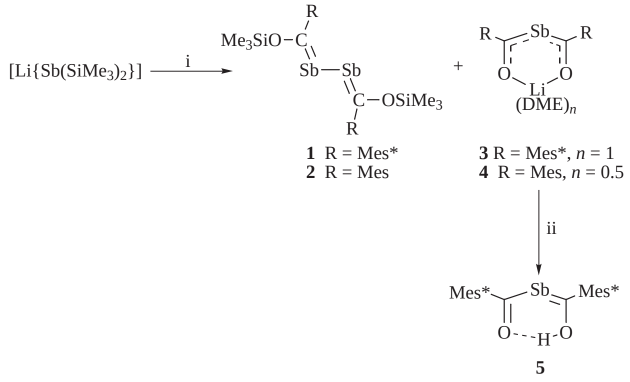


Fig. 1 Molecular structure of Mes*C(O)Sb=C(OH)Mes* **5**. Selected bond lengths (Å) and angles (°): Sb(1)–C(20) 2.078(3), Sb(1)–C(1) 2.192(3), O(1)–C(1) 1.248(4), O(2)–C(20) 1.319(4), O(2)–H(2) 0.96(5), O(1)···H(2) 1.61(5); C(20)–Sb(1)–C(1) 91.31(12), O(2)–H(2)–O(1) 172(5), O(1)–C(1)–C(2) 120.9(3), O(1)–C(1)–Sb(1) 121.2(2), C(2)–C(1)–Sb(1) 118.0(2), O(2)–C(20)–C(21) 117.9(3), O(2)–C(20)–Sb(1) 124.7(2), C(21)–C(20)–Sb(1) 117.2(2).



Scheme 1 *Reagents and conditions:* i, RCOCl, DME, 18 h; ii, R = Mes*, HCl, Et_2O, 0 °C, 2 h.

Compound **5** is stable in toluene solutions for only 15 minutes at room temperature. As a result, spectroscopic data (see SUP 57542) for the compound were collected at 0 °C and are consistent with it existing predominantly in the enol form in this solvent (*cf.* its As analogue[5]). Evidence for this suggestion comes from its ^{1}H NMR spectrum which displays a low field resonance at δ 18.48 in the region normally associated with strongly hydrogen bonded alcoholic protons. The symmetry of this spectrum also suggests that **5** possesses a fully delocalised structure in solution in which the alcoholic proton is undergoing a rapid exchange between the two oxygen centres of the molecule. In the solid state **5** is more thermally stable (decomp. 103 °C) and its crystal structure ‡ (Fig. 1) confirms that it exists in the enol form but with localised Sb(1)–C(20) and C(1)–O(1) double bonds, the former of which compares well with those in **1** [2.056(10) Å][3] and **2** [2.066(5) Å] (see below) but is considerably shorter than normal Sb–C single bonds {*e.g.* 2.225

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† Supplementary data available: synthetic and spectroscopic details for compounds **2**–**5**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/1541/, otherwise available from BLDSC (No. SUP 57542, 4 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

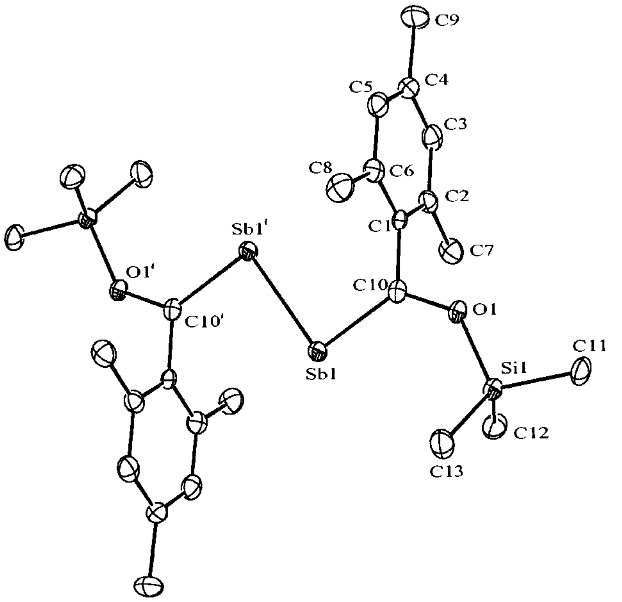

Fig. 2 Molecular structure of $\{Mes(Me_3SiO)C{=}Sb\}_2$ **2**. Selected bond lengths (Å) and angles (°): Sb(1)–C(10) 2.066(5), Sb(1)–Sb(1)′ 2.8018(8), O(1)–C(10) 1.377(5), Si(1)–O(1) 1.697(3); C(10)–Sb(1)–Sb(1)′ 92.99(13), O(1)–C(10)–C(1) 110.6(4), O(1)–C(10)–Sb(1) 125.2(3), C(1)–C(10)–Sb(1) 124.3(3).

(average) in $[Bu^t_3Sb{\cdot}Fe(CO)_4]$[7]}. The acute nature of the C–Sb–C angle in **5** [91.31(12)°] probably results from a significant degree of s-character for the hetero-atom lone pair. This is a common feature of other low coordinate Group 15 systems (*e.g.* RE=ER, E = N, P, As, Sb, Bi) and has been found to be augmented with increasing molecular weight of the Group 15 element.[8] The alcoholic proton H(2) was located from difference maps and refined isotropically. It is bonded to O(2) and appears to have a strong H-bonded interaction with O(1), the angle O(1)–H(2)–O(2) being 172(5)°. As has been suggested for **1**[3] the unusual stability of **5** can probably be attributed to a combination of the steric protection afforded by its bulky aryl substituents and the conjugated nature of the system.

The distibabutadiene **2** (decomp. 105 °C) is not as thermally stable as its more sterically protected counterpart **1** (decomp. 213 °C) but is nevertheless stable in air at ambient temperature for days. Its molecular structure‡ (Fig. 2) is similar to that of **1** and shows it to exist in the *trans*- form with the atoms C(10), Sb(1), Sb(1)′ and C(10)′ being necessarily co-planar. The Sb–C bond length is close to those in **1** and **5** (see above) and as with the C–Sb–C angle in **5** the sharp Sb–Sb–C angles in **2** [92.99(13), *cf.* 94.7(3)° in **1**[3]] can be explained by a high degree of s-character for the Sb lone pairs.

The 2-stibadionato lithium complexes, **3** and **4**, are considerably more stable (**3** decomp. 170, **4** decomp. 103 °C) than the only other example of such a compound, $[\{[Li\{OC(Bu^t)SbC(Bu^t)O\}(DME)_{0.5}]_2\}_\infty]$ **6** (decomp. 65 °C).[5] No crystallographic data were obtained for **4** but in the solid state it probably consists of oxygen and lithium bridged dimeric units linked by non-chelating, bridging DME molecules, as has been found for **6** and a number of related 2-arsa- and 2-phospha-dionatolithium complexes.[5] Compound **3** on the other hand is probably monomeric in the solid state and has its Li centre chelated by a DME molecule, as is the case for its As counterpart.[9] These differences in the degree of association between **3** and **4** would be expected considering the bulk of the aryl substituent in **3**. As is the case for **6**, the symmetry of the solution state ^1H and ^{13}C NMR spectra of **3** and **4** suggest that the ligand backbones of these complexes are delocalised.

We are currently exploring the use of **2** and **5** as ligands in inorganic synthesis and the utility of **3** and **4** as reagents for the transfer of the 2-stiba-1,3-dionate fragments onto other metal centres. We are also investigating the mechanisms of formation of **1**–**4**. The results of these investigations will form the basis of forthcoming publications.

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Notes and references

‡ *Crystal data* for **5**: $C_{38}H_{59}O_2Sb$, $M = 669.60$, orthorhombic, space group *Pcab*, $a = 11.4906(2)$, $b = 20.0826(4)$, $c = 31.2742(5)$ Å, $V = 7216.9(2)$ Å^3, $Z = 8$, $D_c = 1.233$ g cm^{-3}, $F(000) = 2832$, $\mu = 7.94$ cm^{-1}, crystal 0.20 × 0.20 × 0.10 mm, radiation Mo-Kα ($\lambda = 0.71070$ Å), $T = 100(2)$ K, 50378 reflections collected. For **2**: $C_{26}H_{40}O_2Sb_2Si_2$, $M = 684.26$, monoclinic, space group $P2_1/c$, $a = 10.704(2)$, $b = 14.043(3)$, $c = 10.889(2)$ Å, $\beta = 109.57(3)°$, $V = 1542.2(5)$ Å^3, $Z = 2$, $D_c = 1.473$ g cm^{-3}, $F(000) = 1368$, $\mu = 18.48$ cm^{-1}, crystal 0.20 × 0.20 × 0.10 mm, radiation Mo-Kα ($\lambda = 0.71070$ Å), $T = 100(2)$ K, 13007 reflections collected. All crystallographic measurements were made using an Enraf-Nonius Kappa-CCD diffractometer. Both structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[10] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms [except H(2) in **5**] included in calculated positions (riding model). Absorption corrections were carried out using Scalepack.[11] Final R (on F) were 0.0426 (**5**) and 0.0331 (**2**) and wR (on F^2) were 0.0838 (**5**) and 0.0940 (**2**) for $I > 2\sigma(I)$. CCDC reference number 186/1431. See http://www.rsc.org/suppdata/dt/1999/1541/ for crystallographic files in .cif format.

1 K. B. Dillon, F. Mathey and J. F. Nixon, in *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998, and refs. therein.

2 L. Weber, *Chem. Ber.*, 1996, **129**, 367 and refs. therein.

3 P. B. Hitchcock, C. Jones and J. F. Nixon, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 492.

4 P. C. Andrews, C. L. Raston, B. W. Skelton, V.-A. Tolhurst and A. H. White, *Chem. Commun.*, 1998, 575.

5 J. Durkin, D. E. Hibbs, P. B. Hitchcock, M. B. Hursthouse, C. Jones, J. Jones, K. M. A. Malik, J. F. Nixon and G. Parry, *J. Chem. Soc., Dalton Trans.*, 1996, 3277 and refs. therein.

6 S. J. Black, D. E. Hibbs, M. B. Hursthouse, C. Jones and J. W. Steed, *Chem. Commun.*, 1998, 2199.

7 A. L. Rheingold and M. E. Fountain, *Acta Crystallogr., Sect. B*, 1985, **41**, 1162.

8 N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa and Y. Ohashi, *J. Am. Chem. Soc.*, 1998, **120**, 433; N. Tokitoh, Y. Arai, R. Okazaki and S. Nagase, *Science*, 1997, **277**, 78; N. C. Norman, *Polyhedron*, 1993, **12**, 2431.

9 C. Jones and R. C. Thomas, unpublished work.

10 G. M. Sheldrick, SHELX97, University of Göttingen, 1997.

11 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter and R. M. Sweet, Academic Press, New York, 1996.

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